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Rewritable Full Color Photonic Polymer using a Liquid Crystal Ink

Monali Moirangthem,^a Anouk F. Scheers^a and Albertus P. H. J. Schenning^{*ab}

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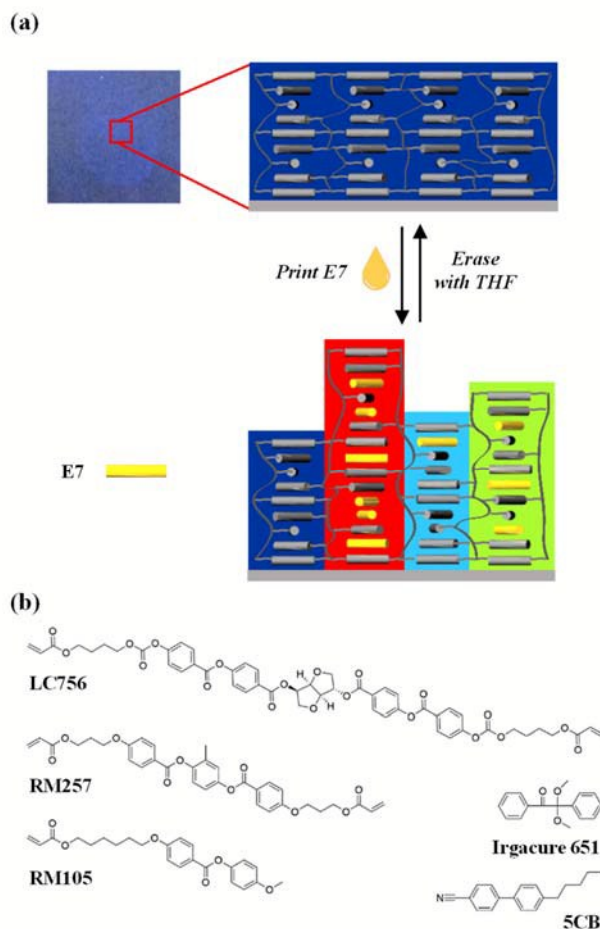
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A printable and rewritable photonic polymer coating has been fabricated from a cholesteric liquid crystal. Full color images can be patterned in the polymer coatings by using a liquid crystal ink. The printed patterns can be erased and rewritten multiple times, making these coatings interesting as rewritable papers.

Beauty of nature is enriched by the abundance of colorful patterns that arise due to photonic structures which are arrangements of periodically alternating refractive indices.¹ The fraction and color of light that is reflected from these multilayers is proportional to the thicknesses and refractive indices of the layers. These structural colors can be found in opal stones, Hibiscus flowers, insects like beetles and butterflies, chameleons, peacocks and cephalopods, *etc.*^{2–5} These natural photonic structures have inspired scientists to fabricate artificial photonic materials for applications such as sensors, security labels, house decors, displays and rewritable papers, using block copolymers, colloidal crystals, or cholesteric liquid crystals (CLC).^{6–10} For example, rewritable photonic materials have been developed from colloidal crystals; however, the stability of the color of the patterns remains an issue.^{11–22} Moreover, these patterns were limited to only two colors. In addition, in most cases the patterns remain invisible under normal conditions and require the aid of solvents such as water, ethanol or vapors for visualization.^{23–27} Fabrication of photonic materials with full color stable patterns in dry environment remains a challenge.

Herein, we report on a photonic coating based on CLC polymer that can be inkjet-printed to obtain a rewritable photonic paper with stable full-color patterns (**Scheme 1a**). A CLC polymer is a one-dimensional photonic material with

molecular helical organization, and the wavelength of light reflected is directly proportional to the length of the helical pitch, making them very interesting for fabrication of responsive photonic materials with ease.^{28–32} The full color patt-



Scheme 1. (a) Schematic showing the working principle of patterning in the photonic polymer coating. (b) Structure of the chemical components used to fabricate the photonic polymer coating.

^a Stimuli-responsive Functional Materials and Devices, and Institute for Complex Molecular Systems, Eindhoven University of Technology, P. O. Box 513, 5600 MB, Eindhoven, The Netherlands

^b SCNU-TUE Joint Laboratory of Device Integrated Responsive Materials (DIRM), South China Normal University, Guangzhou Higher Education Mega Center, 510006, Guangzhou, China

E-mail: a.p.h.j.schenning@tue.nl

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erns were obtained by using a liquid crystal (LC) as ink.

The photonic polymer coating was fabricated from a CLC mixture (**Scheme 1b**) comprising of diacrylate (RM257) and monoacrylate (RM105) mesogens. A chiral dopant that also acts as a cross-linker (LC756) was added to induce CLC phase and a photoinitiator (Irgacure 651) was used to initiate the photopolymerization reaction and freeze the phase. Finally, to introduce patternability to the photonic polymer in a broad range of colors of the visible spectrum, a non-polymerizable cyanobiphenyl LC derivative (5CB) which could be removed from the polymer network was used.⁸ Shearing the CLC mixture in between two glass plates – top one functionalized with methacrylate and bottom one with fluorinated alkylsilane moieties – led to formation of a planarly aligned CLC film, which on polymerization by shining UV light and followed by removal of the top glass plate resulted in a red colored CLC polymer coating ($\lambda \approx 666$ nm) covalently attached to the bottom glass plate (**Figure S1a**). Washing out the non-reactive 5CB mesogen with an organic solvent (tetrahydrofuran, THF) ultimately led to a violet colored polymer coating with reflection band centered at $\lambda \approx 384$ nm (**Figure S1a**). FT-IR spectrum (**Figure S1b**) of the coating revealed disappearance of the peak of the stretching vibration of ($\text{C}\equiv\text{N}$) at 2225 cm^{-1} , revealing complete removal of 5CB.

Removal of the non-polymerizable 5CB led to collapse of the polymer network, reducing the helical pitch length to give the coating a violet color. This also rendered the network highly flexible with enhanced optical response to stimuli.^{8,9} This flexible network could be swollen with E7, which is an LC mixture of cyanobiphenyl and cyanoterphenyl derivatives exhibiting a nematic phase in the broad temperature range from $-10\text{ }^{\circ}\text{C}$ to $58\text{ }^{\circ}\text{C}$.³³ In order to achieve photonic patterns, local swelling of the polymer is essential. To do so, introducing E7 only at the desired areas becomes necessary and the most controlled method of doing this is employing the inkjet printing technique. Therefore, the printability of the polymer coating was first investigated with E7 as the ink.



Figure 1. Photograph of the CLC polymer coating patterned with letters saying "Smile", a smile icon, and a sun by inkjet-printing with E7 as the ink

As E7 is nematic in room temperature, it can be readily filled in an inkjet printer cartridge and printed in droplets of 10 pL in volume. For an ink to be jetted from the cartridge, a viscosity in the range of 10–12 cP is required. However, E7 at room

temperature is highly viscous with viscosity $\approx 224\text{ cP}$.³⁴ Therefore, the cartridge was heated above the isotropic phase transition temperature of E7 at $70\text{ }^{\circ}\text{C}$ to lower its viscosity. In addition, the polymer coating was preheated to $60\text{ }^{\circ}\text{C}$ to enhance the kinetics of swelling. The polymer coating was finally inkjet-printed with drop spacing maintained at $20\text{ }\mu\text{m}$ (1270 dpi) to make a pattern containing letters that say "Smile", a smile icon and a sun (**Figure 1**). The areas where E7 was printed swelled immediately at $60\text{ }^{\circ}\text{C}$, causing an increase in the length of the helical pitch resulting in a color change from violet to orange. Cooling down the patterned polymer to room temperature had no effect on the color of the photonic patterns. The polarized optical microscopy (POM) image of the pattern created showed a sharp contrast between the printed area and the background, implying that there is negligible occurrence of lateral diffusion of E7 into the non-printed area (**Figure S2**). A plausible explanation could be the anisotropy of the CLC polymer network leading to a preferred transverse diffusion. Remarkably, other colors with wavelengths shorter than orange such as green and blue were also present at the edges. This signifies that spacing between the printed drops was too small and they were coalescing at a large scale leaving behind a non-uniform distribution of ink at the edges of the printed areas. However, this also shows that multiple structural colors are achievable with the CLC polymer coating and ink E7.

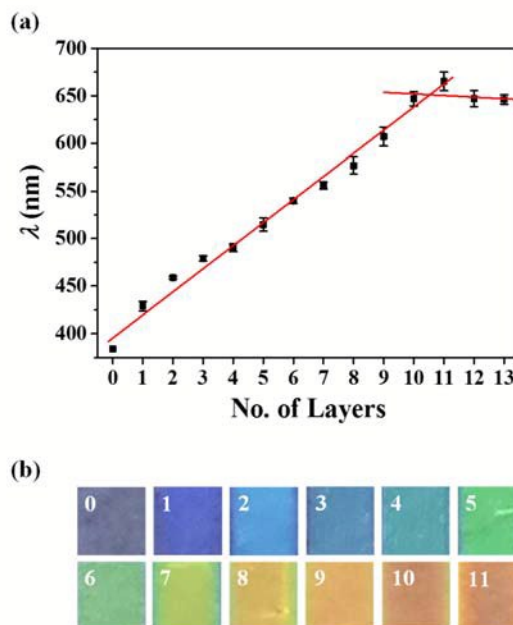


Figure 2. (a) Wavelength of light reflected by the photonic pattern on CLC polymer with different number of layers of ink E7 printed. The red lines represent the linear fitted curves. Error bars indicate mean $\pm$ standard deviations for three measurements at different areas on the pattern. (b) Photographs of the printed patterns with the number representing the number of layers of ink.

To achieve multiple color patterns in the polymer coating, the amount of ink printed per print needs to be reduced. Therefore, the inkjet printer cartridge was replaced with another cartridge that prints droplets of 1 pL in volume. Moreover, the spacing between the drops was increased from $20\text{ }\mu\text{m}$ to $40\text{ }\mu\text{m}$ (635 dpi) and a rectangular pattern of

dimension 1 mm $\times$ 5 mm was then printed with the cartridge heated at 70 °C and the polymer coating pre-heated at 60 °C. Printing the first layer of E7 led to a slight swelling of the network and the much darker violet color ($\lambda \approx 384$ nm) changed immediately into lighter violet ($\lambda \approx 429$ nm) (Figure 2). Printing a second layer resulted in further swelling prompting the color to turn blue ($\lambda \approx 459$ nm). A third layer of ink resulted in a further red shift of the wavelength of light reflected ($\lambda \approx 479$ nm). A fourth layer made the pattern turn bluish-green ($\lambda \approx 490$ nm) while a fifth layer led to a slight red shift to change the color into full green ($\lambda \approx 515$ nm). Printing a sixth layer turned the pattern into lighter green ($\lambda \approx 540$ nm) and a seventh layer made it greenish-yellow ($\lambda \approx 556$ nm). Printing an eighth and ninth layers resulted in yellow ($\lambda \approx 577$ nm) and orange ($\lambda \approx 607$ nm) colors respectively. A tenth layer of ink led to further swelling of the polymer network resulting to red ($\lambda \approx 647$ nm) color. Printing additional layers did not cause any significant changes and the color remained red. These results show that structural colors can be obtained having wavelength ranging from blue to red. On plotting the number of layers against the reflection wavelength, a linear relation is observed up to ten layers and after the tenth printing step, saturation takes place. This indicates that all the ink was absorbed after each printing step and maximum swelling of the polymer network was reached after the tenth step.

After having determined the number of layers required to achieve patterns in full structural colors ranging from violet to red in a dark violet background, an image with three flower plants, such that each has different color petals, pistils, and

stem-leaf, was chosen to demonstrate the fabrication of full color patterns. Figure 3a shows the pattern with the amounts of E7 printed accordingly to obtain the different types of colors. UV-Vis measurement (Figure 3c, Figure S3) showed that the reflection band of the flower petals, labeled as F1, F2, F3 were centered at $\lambda \approx 641, 590, 461$ nm while for the pistils, labeled as P1, P2, P3, it was centered at $\lambda \approx 438, 468, 568$ nm. For the leaves-stems, labeled as L1, L2, L3, the reflection band was centered at $\lambda \approx 488, 530, 505$ nm. Height profile measurement of the red color flower petals F1 showed 67.3 % increase in thickness, and is in good agreement with the observed 67.5 % increase in pitch length of the CLC polymer network (Figure S4).

In order to investigate the effect of time on the color of the patterns, the printed pattern was stored at ambient conditions for a week. On the eighth day, UV-Vis spectra were measured and no significant change was found in the position of the reflection bands of the petals, pistils, or leaves-stems (Figure 3c), implying that the photonic patterns are stable and remarkably durable. Figure 3b shows a photograph of the full color pattern after 7 days of being printed.

To demonstrate rewritability of the photonic polymer coatings, a coating that was patterned in three representative colors – orange, yellow, and bluish green, was erased by treating with THF which dissolved the E7 ink, leaving behind the violet coating with no photonic patterns (Figure 3d). The coating could then be re-printed and erased. Carrying out the print-erase cycle ten times showed similar optical properties of the printed patterns for each cycle (Figure 3e, f).

In conclusion, we have developed a fully rewritable and pri-

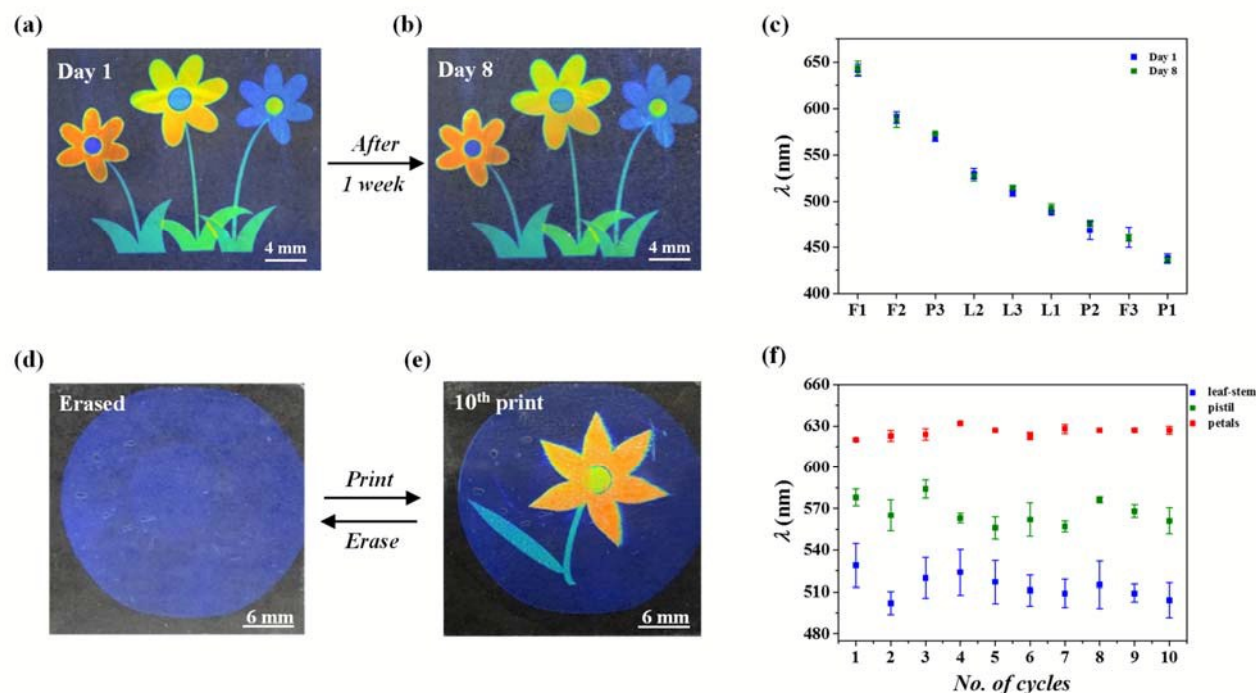


Figure 3. (a) Photograph of an inkjet-printed full color pattern on day 1 of printing. (b) Photograph of the same inkjet-printed pattern after 7 days. (c) Wavelength of light reflected by different color regions of the pattern on day 1 of printing and after 8 days. F1, F2, and F3 represents the red, orange, and blue flower petals. P1, P2, and P3 represents the violet, blue, and yellow pistils. Finally, L1, L2, and L3 represents the leaves-stems of the three flowers. Error bars indicate mean $\pm$ standard deviations for three measurements at different areas on the pattern. (d) Photograph of a polymer coating after erasing printed patterns with THF. (e) Photograph of the same polymer patterned with a flower image printed for the tenth time after 9 print-erase cycles. (f) Wavelength of light reflected by the different color parts of the flower patterns which had been printed successively after erasing the previous one. Error bars indicate mean $\pm$ standard deviations for three measurements at different areas on the pattern.

ntable photonic coating from a CLC polymer network. The coating could be inkjet-printed with E7 mixture as LC ink to locally swell the network and create patterns of colors ranging from violet to red which are visible without the use of a solvent or vapor. The printed patterns were stable and durable in ambient conditions, and could be erased completely to print another new pattern. The range of colors can be further tuned by varying the amount of the non-polymerizable mesogen initially present in the network making these photonic polymer coatings appealing as rewritable photonic papers. Furthermore, by using LC inks which are polymerizable, it will be possible to fabricate arbitrary polymer patterns which can, for example, change colors and topographies in response to a stimulus.^{35,36}

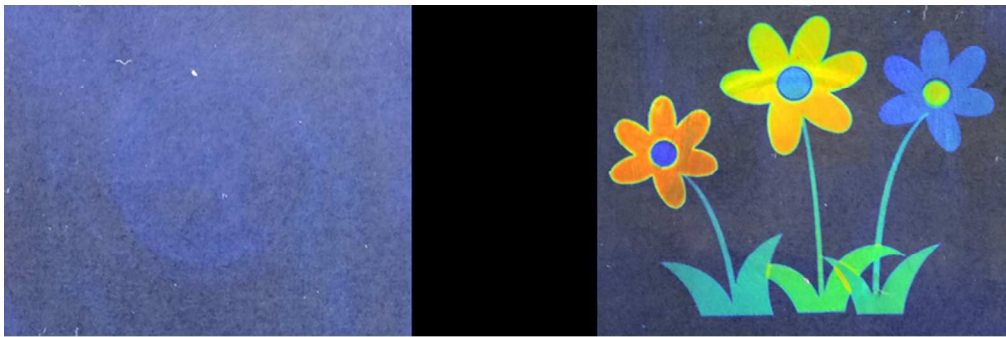
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Conflicts of interest

There are no conflicts to declare.

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